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I. Time Reversibility Concepts, the Second Law and Irreversible Thermodynamics

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Abstract. Time reversibility concepts and transformations are first reviewed and difficulties with the standard formulations indicated. The kinetic equations which were constructed to exhibit reciprocity relations in their transition probabilities based on time reversal ideas are examined next and a first principle analysis shows that the standard forms are not in accord with the first principles. A thermodynamical theory based on the Kelvin-Clausius-Planck definition of entropy and a modified form of the Benofy and Quay postulate concerning conductive heat is developed and reciprocity and other relations are derived as an example of one possible alternative to the standard treatments with their indicated inconsistencies.

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INTRODUCTION

This work briefly touches on some aspects of mechanics connected to time reversibility and how it has impinged on the formulation of physical theories, especially those connected to rate laws and thermodynamics, especially the Second law. It is a partial resume of what appeared in Apeiron journal (where some of the equations and labels were sadly erroneously typeset by the publisher [1]). The heart of the problem and paradoxes in thermodynamics lies the the belief of the founding fathers of this field that the laws of mechanics and electrodynamics are reversible. The list of eminents include Loschmidt, Maxwell, Clausius [2], Tolman [3], Feynman [4, Ch.5: *The distinction between past and future*], Einstein, Prigogine [5, 6] and the cohesive, well-funded and influential fraternity involved in the creation of CPT symmetry physics and particle physics [7]. We also comment briefly on the master equation method and illustrate a method of constructing irreversible systems with reciprocity behavior based on extending a concept of heat conduction first developed by Benofy and Quay [8]. The concepts of time reversibility, detail balance, system evolution and entropy are closely connected, where time reversibility assumptions stem from considerations in mechanics, whilst all the latter phenomena are often described as a marriage of mechanics with statistical theories. We will touch on these topics based on the above sequence of theoretical interdependencies.

Classical mechanical description

There are two basic mechanical principles [3, p.102], (i) the principles of dynamical reversibility and (ii) reflectability which underpin current descriptions of irreversibility, and in thermodynamics, the development of the entropy formalism contained in the Boltzmann H-Theorem [9, paragraph about eqn. (14] and various fluctuation-dissipation theorems and their quantum analogues attributed to Callen and co-workers [10, p.173]. The principle of dynamical reversibility states [3, p.102] that by suitable choice of initial conditions for conservative Lagrangians or Hamiltonians symmetric in their momenta, there exists two solutions to the equations of motion, $(-t,q,-p)$ and (t,q,p) where $t,q,$ and p are the time,position and momentum coordinates respectively, whilst the principle of dynamical reflectability states (in Euclidean space, Cartesian coordinates) that for positive time, there exists independent solutions (x,y,z) and $(x,y,-z)$ for these systems of coordinates. The importance of these statements for many particle thermodynamics is that for steady state conditions where there is a net particle flux, there exists an average potential due to the structure of the system $V(x_i)$ for particle flux species x_i, and thus the above principles are applicable to the average motion of particles, which yields the detail-balance condition [11, 12] [13, pp. 35-39] which some consider more fundamental then the Second law [14]. There exists also an average force-field $\langle -V(x_i)\rangle$ where symmetry conditions are imposed for the case of dynamic reflectability. We assume unit mass here and the Hamiltonian H having the form $H(\mathbf{p},\mathbf{q}) = T(\mathbf{p}) + V(\mathbf{q})$ where T is the kinetic energy and V the potential energy. Hamilton's equations of motion $\dot{\mathbf{q}} = \partial H/\partial \mathbf{p}, \dot{\mathbf{p}} = -\partial H/\partial \mathbf{q}$, are said to be invariant for the transformed variable set $T \equiv \{t' = -t, \mathbf{q}' = \mathbf{q}, \mathbf{p}' = -\mathbf{p}, H' = H(\mathbf{p}',\mathbf{q}')\}$ where the primes are for the transformed variables, and both these motions at $(\mathbf{p},\mathbf{q})$ and $(\mathbf{p}',\mathbf{q}')$ must also represent the same acting force field since

$$\dot{\mathbf{p}}' = \dot{\mathbf{p}} = -\partial H'/\partial \mathbf{q}' = -\partial H/\partial \mathbf{q} = \mathbf{F} = \mathbf{F}' \tag{1}$$

Newton's law on the other hand yields $\mathbf{F} = d\mathbf{p}/dt$, whereas by reversing $\mathbf{p}$, $d\mathbf{p}'/dt = -\mathbf{F}$ for the positive time increment dt. This apparent paradox is resolved by noting that the set T above is a re-parameterization of the same unique equation of motion, where if $t' = -t$, $\mathbf{F}' = d\mathbf{p}'/dt' = \mathbf{F}$, so that for any point in positive time, there is only one non-superimposible solution, implying a vector direction in the transformation which is depicted below in Fig.(1). In practice, however, the principle is evoked for positive time increments, with the superposition of two different solutions for fixed t so as to yield the desired results [15, p.55 Sec 4], [16, Sec 46-3 to 46-9], [17, pp.3,4,47,73,104,149,etc.] [6, pp.2,6,203],[18, p.121] and from the above does not generally obtain from the algebra and therefore is an assertion. An explanation of the Hamiltonian mechanics follows below in Fig.(1). The points in the T transformation may be represented by a line diagram below representing a particle trajectory in real (positive) time in direction OX, whereas negative time is along OX' by "time reversal". The trajectory AB is mapped by T to the line path A'B'(i.e. not B'A', which is a translation over positive time increment δ). Thus, the computation of trajectories cannot imply independent solutions to the Hamiltonian which give rise to differences in physical properties such as the motion as alleged in the development of this asserted principle. Referring to Fig.(1), if by path

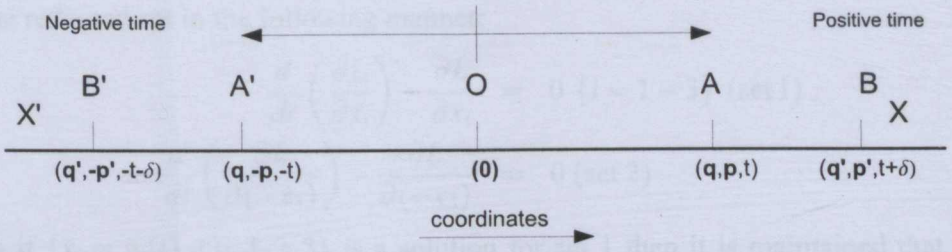

FIGURE 1. The mapping of the unique trajectory in positive time A $\longrightarrow$ B follows the unique vector in so-called negative time from A′ $\longrightarrow$ B′. .

1 the system is at point $(\mathbf{q},\mathbf{p})^1$ initially in Γ space (point A), then at time $t(=\delta)$ *later* it is at some point $(\mathbf{q}',\mathbf{p}')^1$ (point B) which is uniquely related to $(\mathbf{q},\mathbf{p})^1$ by Hamilton's equations along the vector AB. If initially it has coordinates by path 2 $(\mathbf{q}',-\mathbf{p}')^2$ (point B',and where the same symbol for the coordinates represents the same numerical value) then at time increment t later $(=\delta)$ in positive time, it may be represented at point $(\mathbf{a},-\mathbf{b})^2$, where if the vector line trajectory of the diagram is maintained, then it does not follow that $\mathbf{a}=\mathbf{q}$, and $-\mathbf{b}=-\mathbf{p}$ as assumed in the standard development, e.g. [18, p.121] since this would violate the equivalence of Newtonian and Hamiltonian mechanics as proved above since the AB line trajectory is equivalent to the A'B' line trajectory under time reversal invariance and not B'A'. Another fundamental example of the time reversal T transformation is in the original and subsequent quantum development [19, p.521] of the Boltzmann collision integral where the scattering cross-section s referred to molecules 1 and 2 with initial velocities $\mathbf{v}_1$ and $\mathbf{v}_2$ (prime denotes final velocities after scattering) written $s'(\mathbf{v}_1,\mathbf{v}_2\rightarrow\mathbf{v}_1',\mathbf{v}_2')$ corresponding to AB in the diagram is equated to $s'(-\mathbf{v}_1',-\mathbf{v}_2'\rightarrow-\mathbf{v}_1,-\mathbf{v}_2)$ representing line B'A', violating the specified vector direction of the transformation. Tolman opines that since dynamics involves both spatial and time coordinates, inverting their axis should lead to conservation properties. His inverting the time axis assumes the fallacy of the above concerning the vector direction of the transformation; he calls the consequences of the time reversal operation the principle of "'dynamical reversibility"' [3, Sec. 37(a)] whereas the other principle is called the principle of dynamical reflectability [3, Sec. 37(b)] which we consider next.

Principal of dynamical reflectability

From the above, for the stated Hamiltonian, two distinct solutions do not exist in positive time. It is also possible to make this conclusion from the proof of this supposed principle, as given by the treatises [3]. For Lagrangian systems with the above stipulated

conditions (including the potential V being an eigenfunction and also a function of the coordinates), the proof of the principal is to compare the Euler-Langrange (EL) equations for a particle trajectory for all three coordinates (set 1) with another (set 2) with the same form except that one of the coordinates, say the x_3 coordinate be replaced by the reflected set in the following manner:

$$\begin{aligned} \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{x}_i}\right) - \frac{\partial L}{\partial x_i} &= 0 \ \{i = 1-3\} \ (\text{set } 1) \\ \frac{d}{dt}\left(\frac{\partial L}{\partial(-\dot{x}_3)}\right) - \frac{\partial L}{\partial(-x_3)} &= 0 \ (\text{set } 2) \end{aligned} \tag{2}$$

Then if $\{x_i = g_i(t), i = 1,2,3\}$ is a solution for set 1 then it is maintained that $\{x_i = g_i(t), i = 1,2, x_3 = -g_3(t)\}$ [3, Sec. 37(b)] must also be a solution. However, for Langrangians symmetrical in the velocity variables, the $i = 3$ (set 2) equation is equivalent by multiplication by -1 to the $i = 3$ (set 1) equation for the same time variable t so that a distinct solution is not anticipated but Tolman opines that the importance of this principle is that it envisages a plane of reflection, so that for a specified motion, [3, Sec. 37(b)] "*any motion of a system and any mirror image or enantiomorph of that motion would be equally possible*" . Thus, violations in handedness would be said to exist when experiments do not show equal proportion of measured intensities of properties arising from enantiomorphic motion. Furthermore, such interpretations would justify Onsager setting the equality to the following correlation function [10, p.76]

$$< x_1(0)x_2(t) > = < x_1(0)x_2(-t) > \tag{3}$$

where other statistical developments demand transforms which set as negative both momentum and time to preserve time reversibility. If the forces are specified for the particle motion at each infinitesimal segment of the true path, then for the kth particle, the co-ordinate $\mathbf{r}_k$

$$\mathbf{r}_k = \int^t \int^{t'} \mathbf{F}_k(t'')dt''dt' \tag{4}$$

so that two arbitrary constants (e.g. the position and momentum) is sufficient to uniquely define the path. Since $\mathbf{F}_k$ does not change sign upon reversing the momentum or velocity in negative time, there can be only one unique path in both negative time and positive time - where the two times are parameters of each other (to two arbitrary constants)- which contradicts the standard assumptions [13, p.81]. The quantum analogues of detailed balance follow a similar form of reasoning as is found in classical derivations and may be similarly examined. In the Onsager theory of linear irreversible thermodynamics (LIT), the entropy deviation from equilibrium ΔS as a result of a displacement of thermodynamical variables a_i is [11, 12], [19, pp.36-41]

$$\Delta S = -1/2 \sum_j \sum_i g_{ij} a_i a_j. \tag{5}$$

The thermodynamical forces F_i are defined as

$$F_i = \frac{\partial \Delta S}{\partial a_i} = -\sum_j g_{ij} \tag{6}$$

where $< a_i F_i >= -k\delta_{ij}$ and δ_{ij} is the Kronecker delta. The linear approximation gives

$$\dot{a}_i = \sum_j p_{ij} a_j \quad \text{or} \quad \dot{a}_i = \sum_j L^*_{ij} a_j \tag{7}$$

where $\dot{a}_i$ is actually a "fluctuational" derivative defined by

$$\dot{a}_i = < a_i(t+\tau) - a_i(t) > / \tau \tag{8}$$

where τ is said to be larger than the relaxation time for molecular interactions but smaller than the time for the regression of the fluctuation. The entropy production is given by

$$\dot{S} = \sum_i \dot{a}_i F_i \tag{9}$$

where $\dot{S} = \dot{\sigma} \geq 0$ by the "'Second law"', where the "'internal"' entropy production is $\dot{\sigma}$ and for any volume element, the total entropy production increment is said to be $dS' = d_e S + d_i S$ where $d_e S$ is the entropy brought from the outside and $d_i S$ the energy created from "'inside"'. We show this violates the Kelvin-Clausius-Planck (KCP) definition of entropy. If flows are defined in terms of (8) then the Onsager coordinates are defined to be properly chosen and reciprocity $L^*_{ij} = L^*_{ji}$ is assured where

$$\dot{\sigma} = \sum_i \dot{a}_i F_i = \sum_{ij} L^*_{ij} F_i F_j \geq 0 \tag{10}$$

and where $\dot{\sigma}$ is determined from Gibbsian thermostatic entropy and balance equations. The assertion of time reversibility demands [13, p.36]

$$\langle a_j(t+\tau) \rangle = \langle a_j(t-\tau) \rangle . \tag{11}$$

From (11) assuming weak couping and the assertion, we get

$$\langle a_i(t) a_j(t+\tau) \rangle = \langle a_i(t) a_j(t-\tau) \rangle . \tag{12}$$

Making use of further weak coupling assumptions, we get from (7-8) and the above

$$\langle a_j(t) a_i(t+\tau) \rangle - \langle a_j(t) a_i(t) \rangle = \tau k L^*_{ij} \tag{13}$$

$$\langle a_i(t) a_j(t+\tau) \rangle - \langle a_i(t) a_j(t) \rangle = \tau k L^*_{ji} \tag{14}$$

In order to derive the reciprocity condition $L^*_{ij} = L^*_{ji}$ it is necessary to force the identity

$$\langle a_j(t) a_i(t+\tau) \rangle = \langle a_i(t) a_j(t+\tau) \rangle \tag{15}$$

in (13-14). This is achieved by supposing that it is permissible from "the postulates of statistical mechanics" to substitute $t+\tau$ for t on the the right hand member of (11) whilst supposing that the left hand member need not be similarly substituted [13, p.36]. Apart from the time reversibility assumptions leading to (11), this argument seems to raise several difficulties. The $< a_i(t) >$ are stochastic variables that might

differ for each point in time since they measure the change of the variable during the regression of a fluctuation towards equilibrium and are therefore not time independent for stochastic variables in "aged" systems. Thus, shifting times on one member of (15) implies a translation of the distance of the coordinate from equilibrium corresponding to a different value range of the thermodynamical forces, which contradicts the initial assumption. From what has been mentioned, it is therefore possible to map a coordinate (scalar) time point t, with respect to a regression from equilibrium, such that (in the steady state) the equation $\hat{\mathbf{T}}(\mathbf{F}) = t$ is a scalar product and $\mathbf{F}$ is the thermodynamic force vector and $\hat{\mathbf{T}}$ an operator.

The extension to quantum mechanics is currently dependent on the validity of 'microscopic reversibility' in the sense that Newton's laws or Hamiltonian dynamics do not imply irreversibility, and this type of conviction appears to be the basis on which E.P. Wigner [20, Chap.26], Schwinger and others [21, Chap.4] developed a theory of time reversal in quantum mechanics and applied them to physical systems, such as in particle physics and those attributed to degenerate levels (Kramer's degeneracy) [22, pp.166,193-196] in atomic spectra [20, Chap.26]. If it were true that Newton's laws of motion were "reversible" in this commonly assumed sense, then the Onsager 'principle' that both directions of a thermodynamic path are traversed with equal frequency (microscopic reversibility hypothesis) in any physical system would seem a most reasonable assumption in equilibrium at least, because of the "neutrality" in the direction of motion given a fixed force field configuration. Since this is not generally the case, then the current thermodynamical developments in at least the Callen, Onsager [23], Prigogine [5] and particle physicist sense may be opened to question. Wigner time reversal in quantum mechanics is achieved by supposing that the diagonal elements of Hermitian operators have classical analogues, that is, that the expectation values of certain quantum mechanical operators such as for momentum and position corresponds to the classical behaviour of systems within the appropriate limits. For instance, under the time reversal operator, $\hat{T}$ the following are assumed to result for the expectation values of a quantum mechanical system, i.e.

$$x \xrightarrow{\hat{T}} x,\ p \xrightarrow{\hat{T}} -p, L \xrightarrow{\hat{T}} -L, \text{ and } t \xrightarrow{\hat{T}} -t \tag{16}$$

where x, p, L and t represents the position, momentum, angular momentum and time co-ordinate respectively [21, p.82]. These quantities would yield new properties as a result of 'time reversal'. The influence of these "principles of time reversal invariance" has been deep and far reaching in particle theory where it constitutes the fundamental means of analyzing nuclear processes. In particle physics, the ideas of "symmetry violations" are based on such ideas as space and time invariances and reversals [7, pp.16-20]. We would like to propose that such a type of assumed procedure with regard to classical time reversal (and possibly other) invariances have led to an interpretation of nature where symmetry and symmetry violations have become the basis for postulating theorems in particle physics, technically known as CPT symmetry principles [7, p.16] and in irreversible thermodynamics. Perhaps the "element of surprise" which accompanied the results of the decay of Co^{60} was in part conditioned by the inherent belief in the symmetry properties of the Hamiltonian as explained by Tolman concerning enantiomers, including its "time reversed" properties [7, p.4] as again outlined in the Tolman expositions. The incorporation of "time reversal" adds yet another mathematical property to

the resulting equations, where the transformation of the Hermitian operators under say parity has a form not dissimilar to those for time reversal [21, p.81 eqns 4.7-4.10]. This would introduce all kinds of properties which may be correlated and contrasted to experimental results, leading to the apparent violations etc. In quantum theory, time reversal ideas have been applied to the commutation relations between coordinates and momentum to keep them invariant with respect to time reversal, and one has to choose the time reversal operator that facilitates such operations: in retrospect, one can observe that entire schools of algebra and many distinguished careers have been launched as a result of the influence of these ideas of time reversibility.

Example of ensemble theory and transition probabilities

We show by comparing our results derived from first principles with very standard and well established developments based on detailed balance, time reversibility and reciprocity of the transition probability matrix λ_{ij} indices [24] that there is no compatibility for the transition probability expression. We use the standard notation of set theory in our evolution equations [25] where events separated in time by the time parameter t in any one frame of reference may be viewed as constituting separate classes of these same events at different times, where these events form non-empty set classes denoted by $A_1, A_2 ... A_n; B_1, B_2 ... B_n$ and so on in the time domain (denoted by subscripts) of mutually exclusive events. Thus,we write for the probability of event A occurring at time t denoted by $P(A(t))$ the following expression

$$\begin{aligned} P[A(t)] &= \sum_k P(A|B_k(t-\delta t)).P[B_k(t-\delta t)] \\ &= \sum_k P[A(t)]P[B_k(t-\delta t)] \end{aligned} \tag{17}$$

Here, the events $B_1, B_2 ... B_r$ precede event A and they form a complete set of events from which event A may arise after time δt. Suppose we prepare N identical systems at time $t' = 0$ and examine them at time t. Let the number of systems with quantum numbers r and q (where r and q may represent a vector of quantum numbers) at time t be denoted by $\varepsilon_{r,q}$. Then, relative to the initial state, we define the probability (if the limits exists) of the state $\chi(r,q)$ at time t as

$$P_{rq}(t) = \lim_{\varepsilon, N \to \infty} (\varepsilon_{r,q}/N). \tag{18}$$

If only one system were prepared and we determine after time t the state of that system (having the same initial state as the above ensemble) and repeat the procedure N' times, then we may define the probability of the system to be in the state $\chi(r,q)$ at time t as

$$P'_{rq}(t) = \lim_{\varepsilon', N' \to \infty} (\varepsilon'_{r,q}/N') \tag{19}$$

where $\varepsilon'_{r,q}$ is the number of times the system is in state $\chi(r,q)$ after time t within the set of N' measurements. A common postulate of statistical mechanics asserts (Gibbs'

Ergodic theorem) that for distinguishable systems

$$P'_{rq}(t) = P_{rq}(t). \tag{20}$$

The term $\varepsilon_{r,s}$ represents the number of trajectory lines that puncture the region that belongs to the state $\chi(r,s)$. For what follows, we assume that the appropriate limits have been taken (the ε's and N's all tend to infinity); further $\varepsilon^{\phi,\xi}_{\alpha,\beta}$ represents the number of system trajectories which puncture the state set $\chi(\alpha,\beta)$ at time t and end up finally in the quantum state $\chi(\phi,\xi)$ in the further (unit) time δt. The subscripted variables represent the initial trajectory class and superscripts the final trajectory destination for any time interval (δt). For what follows, the λ transition probabilities and ε's are all functions of time unless otherwise indicated. The change in probability δP_{rs} of the system being in the state $\chi(r,s)$ between time t and $t+\delta t$ is then given by

$$\delta P_{r,s} = \Delta\varepsilon r,s/N = -1/N\{\varepsilon_{r,s}(t) - \varepsilon_{r,s}(t+\delta t)\}. \tag{21}$$

From (17-21) we write the transition probabilities λ as

$$\begin{aligned} \lambda_{rs,qz}(t) &= \varepsilon^{q,z}_{r,s}(t)/\varepsilon_{r,s}(t) \\ &= P^{q,z}_{r,s}(t)/P_{r,s}(t) \end{aligned} \tag{22}$$

where we define $P^{q,z}_{r,s} = \lim_{N\to\infty} \lim_{\varepsilon^{q,z}_{r,s}\to\infty} \varepsilon^{q,z}_{r,s}/N$.

From (21), the total number of trajectory lines puncturing the state $\chi(r,s)$ at time $t+\delta t$, $\varepsilon_{r,s}(t+\delta t)$ must be given by:

$$\varepsilon_{r,s}(t+\delta t) = \sum_{\alpha}\sum_{\beta} \varepsilon^{r,s}_{\alpha,\beta}(t) \tag{23}$$

where

$$\Delta\varepsilon_{r,s}/N = -\varepsilon_{r,s}/N + \left(\sum_{\alpha}\sum_{\beta} \varepsilon^{r,s}_{\alpha,\beta}\right)/N. \tag{24}$$

From (22) and (24) we derive

$$\delta P_{r,s} = -P_{r,s}(t) + \sum_{\alpha}\sum_{\beta} \lambda_{\alpha\beta,rs}.\varepsilon_{\alpha,\beta}(t)/N. \tag{25}$$

From (22) and (23), the conservation of the number of systems and the definition for the ε's, we have

$$\begin{aligned} P_{r,s}(t) &= \sum_{q}\sum_{z} \varepsilon^{q,z}_{r,s}/N \\ &= (\varepsilon_{r,s}(t)/N).\sum_{q}\sum_{z} \lambda_{rs,qz}. \end{aligned} \tag{26}$$

Thus, from (25) and (26)

$$\delta P_{r,s} = -P_{r,s}(t)\sum_{q}\sum_{z} \lambda_{rs,qz} + \sum_{\alpha}\sum_{\beta} \lambda_{\alpha\beta,rs}P_{\alpha,\beta}(t) \tag{27}$$

which is similar to the standard thermodynamical expression[24, eqs. 1-2] for the master equation

$$\dot{P}_i = \sum_j (P_j - P_i)\lambda_{ij} \text{ or } \delta P_i = \left(\sum_j (P_j - P_i)\lambda_{ij}\right)\delta t . \tag{28}$$

Transitions in coupled systems. For applications of the above, we consider the coupled transitions, such as that of a system in state i coupled to a heat bath (reservoir or some other system) with quantum state p; let there be a transition of the system to state j, and the heat bath to state r. The transition probability is given (in unit time) by $\lambda_{ip,jr}$. The total transition per unit time from state i to state j of the system (for all values of p and r) is given by $\lambda_{i,j}$. According to the standard representation of the master equations [24, p.242] the following relations must hold:

$$\begin{aligned} \lambda_{ij} &= \sum_r \dot{\sum_s} P_r' \lambda_{ir,js} \\ &\text{where} \\ \lambda_{ji} &= \sum_r \sum_s P_s' \lambda_{js,ir} \\ &= \sum_r \sum_s P_s' \lambda_{ir,js} \quad (\neq \lambda_{ij}) \end{aligned} \tag{29}$$

$$\dot{P}_i = \sum_j \lambda_{ji} P_j - P_i \lambda_{ij} \text{ and } \lambda_{ir,js} = \lambda_{js,ir} \tag{30}$$

where the primed quantities refer to the reservoir states. The state of the combined system is given by $\chi(i,r)$ where it is supposed that if the interaction Hamiltonian between the system and the reservoir is very small in absolute energy, then the state of the system is given by the quantum state i of the system and the quantum state r of the reservoir (usually a product state ij). The probability of the system being in state j, denoted P_j is defined as $P_j(t) = \left(\sum_s \varepsilon_{j,s}(t)\right)/N$ where $\varepsilon_j(t+\delta t) = \sum_q \sum_p \sum_r \varepsilon_{q,p}^{j,r}$ and $\varepsilon_{q,p}^{j,r} = 0$ if there is violation of conservation of energy, for the reservoir-system is closed with a fixed energy. From our own definition of transition probabilities (22) and conservation of systems the following sets of equations must obtain

$$\lambda_{ji} = \sum_p \sum_x \varepsilon_{j,p}^{i,x} / \sum_s \varepsilon_{j,s}(t) \quad ; \quad \lambda_{ij} = \sum_p \sum_x \varepsilon_{i,p}^{j,x} / \sum_s \varepsilon_{i,s}(t) \tag{31}$$

$$\sum_i \sum_s \varepsilon_{i,s}(t) = N \quad ; \quad \sum_i \sum_p \sum_j \sum_x \varepsilon_{i,p}^{j,x} = N \tag{32}$$

where we also define $W'_{ij} = (\sum_p \sum_x \varepsilon_{i,p}^{j,x})/N$ and write $W'_{ij} = \lambda_{ij} P_i(t)$. Then from (31) and the definition of W'_{ij} the total change δP_j in the probability of state j in unit time δt is given by

$$\delta P_j(t) = -\sum_i (W'_{ji} - W'_{ij}) = \sum_i (P_i \lambda_{ij} - P_j \lambda_{ji}) \tag{33}$$

which is somewhat similar to the master equation given by standard treatments in (28). However, since

$$\lambda_{rs,qz} = \varepsilon^{q,z}_{r,s}/\varepsilon_{r,s} \text{ where } \varepsilon_{r,s} = \sum_{\alpha}\sum_{\beta}\varepsilon^{\alpha,\beta}_{r,s}, \tag{34}$$

asserting the standard reciprocity relation has this implication

$$\lambda_{rs,qz} = \lambda_{qz,rs} \Rightarrow \varepsilon^{q,z}_{r,s}\varepsilon_{q,z} = \varepsilon_{r,s}\varepsilon^{r,s}_{q,z}. \tag{35}$$

However, the standard thermodynamical result from Cox (op. cit.) is

$$\begin{aligned}\lambda_{ji} &= \sum_{r}\sum_{s}P'_s\lambda_{ir,js} = \sum_{r}\sum_{s}P'_s\lambda_{js,ir} \\ &= \sum_{r}\sum_{s}\left(\varepsilon^{ir}_{js}/\varepsilon_{js}\right).P'_s\end{aligned} \tag{36}$$

The reservoir state probability is given by $P'_s = (\sum_j \varepsilon_{j,s})/N$ and substituting this in (36) leads to the standard [24] result λ^s_{ji} where

$$\lambda^s_{ji} = \left(\sum_{q}\sum_{r}\sum_{s}\left(\varepsilon^{ir}_{js}/\varepsilon_{js}\right).\varepsilon_{qs}\right)/N \tag{37}$$

and we note that (37) is *not* the same form as out analytic form of (31) $\lambda_{ji} = \sum_p\sum_x \varepsilon^{i,x}_{j,p}/\sum_s \varepsilon_{j,s}(t)$. Thus for modeling kinetic processes, the forms given in (31) must be used if time reversibility assumptions are not utilized whilst the standard forms always assumes such symmetry [24, p.242]. Often, applications have assumed the validity of time reversed detailed balanced without further question.

Example of derivation of reciprocity relations on a physical basis without time reversibility assertions

It was demonstrated [26, 27] by a Gedankenexperiment that the heat Q absorbed by a non equilibrium steady state could be measured during a transition between states and that for a system of fixed volume (no PV work) $dS = dQ/T$ is a perfect differential. Then, describe this entropy as $S = S(\mathbf{X},\mathbf{N},\mathbf{J},\mathbf{Q})$ where S refers to the entropy per unit volume; $\mathbf{X}$ denotes the conventional thermodynamical variables such as temperature T and pressure P and their gradients, $\mathbf{N}$ the variables pertaining to species concentration, $\mathbf{J}$ the flux variables and $\mathbf{Q}$ the source and sink variables for the system. Now, let $\mathbf{R}$ refer to the spatial (or position) variable in a steady state system. Then for each displacement $\mathbf{dR}$, all the other variables would alter by $\{\mathbf{dX},\mathbf{dN},\mathbf{dJ},\mathbf{dQ}\}$. Since [26, p.90, eq.(4a)] $\oint dS = 0$, we can draw any closed loop inside a non-equilibrium system, and about the geometrical loop with coordinates $\mathbf{R}$, we also have

$$\oint_{\partial\mathbf{R}} dS = 0 \tag{38}$$

for any closed loop $\partial\mathbf{R}$ *inside* the system. Previous work attempting to derive reciprocity outside of the above considerations has been found to be ambiguous [26, 28] and illustrates the subtle nature of non-equilibrium theory, including the importance of conductive heat [29] in irreversibility and heat flow direction, a point ill considered in putative derivations (which often seem to possess a spirit of hasty, ambiguous, subsuming and centralizing generality). These apparent derivations simply attempt to derive reciprocity without a physical basis by merely specifying a potential form, where reciprocity conditions obviously must be satisfied in Maxwellian potential theory no matter what the physical process by virtue of the properties of an exact differential and the commutative nature of partial derivatives. Of importance in Physics are the actual processes involved. Here, we do not develop the relations based on envisaging entropy as some type of fluid-like vector. We recall that the Kelvin-Clausius-Planck (KCP) statements of the Second law all refer to the global situation of the transfer of various amounts of energy called "heat" between the reservoirs and a thermodynamic system. There is a fixed temperature parameter within the entire volume which comprises the thermal reservoir by definition, and the entropy increment δS_{KCP} is defined as $\delta S_{KCP} = \delta Q/T = (\int_{\partial C} \mathbf{J_q}.dSdt)/T$ where dt is the increment of time, T the temperature, $\mathbf{J_q}$ the conductive heat vector and dS the surface area increment of the reservoir. Conversely, the imputation of temperature at an instant of time requires spatial extension to accommodate system ensembles which may interact with each other. Changes in definition and meaning occur when other entropy forms, in an *ad hoc* way are introduced. By analogy with fluid dynamics etc., "entropy" was envisaged as a fluid-like vector quantity [30], [11, p.421,eq. 5.7],[31, pp.19-20],[32, Chap.4] given as $\mathbf{J_s} = \mathbf{J_q}/T$ where $\mathbf{J_q}$ is a heat flow term. Then one can construct the quantity $\dot{\sigma}$ the rate of (internal) entropy production where the following balance equation is valid for all times [30] $\partial(\rho.s)/\partial t = -\nabla.\mathbf{J_s} + \dot{\sigma}$ where ρ is the density and s the specific entropy. A careful reading of Callen [30] and all the others show that they actually identify $\dot{S}$ (the rate of entropy production) with $\dot{\sigma}$ at the steady state, which is precisely the Yourgrau position also [13]. From the above discussion, on the other hand, the requirement of spatial extension demands that at the steady state, the temperature distribution along any system must be represented by a three dimensional (Heavyside) step function, so that for a system with N volume elements each designated i, the entropy increase in the steady state can only be $\Delta S = \sum_i^N Q_i/T$ where Q_i are the increments of heat absorbed from each of the elements i. Fourier heat conduction in metals where other cross effects are present such as the flow of electrons subjected to electric and magnetic fields have been treated by separating the different forms of heat flow [30]; where convective heat flow terms may be separable from the "lattice thermal conduction", although from the elementary theory of Linear Irreversible Thermodynamics (LIT) the material property coefficient is altered by cross-effects [30]. More complex LIT systems simply extend this separability of thermal energy flow to all the particle quantities concerned, so that heat conductivity has been defined by Callen as "*the heat current density per unit temperature gradient for zero particle current*" [30]. This theme of net zero particle current is also developed in treatments of kinetic theory dealing with say Fourier heat conduction where the convective heat of transport is considered to be of a different effect from the conductive heat [30] even in the steady state. We will develop a theory

where conductive heat is a collective term involving heats of transport as well as lattice conduction which does not accord with the above separation of terms where we make use of the modified Benofy and Quay (BQ) conjecture concerning conductive heat. It has been shown [29] that the BQ effort to base a rigorous theory of irreversible (thermomagnetic) phenomena via the Fourier Inequality is not quite correct because the heat terms were misconstrued. However, it was pointed out that if the "conductive" part of the heat transfer is considered (in the Callen sense), then the Fourier Principle in relation to conductive heat flow is (unless proven otherwise) a general statement not immediately derivable from the Second law (though not violating it). In what follows, [33] we confine ourselves to systems which are comprised of particles or quasi-particles which exchange momentum according to Newton's conservation law, or else a modification of the meaning of temperature and the Boltzmann coupling constant is required [33]. We redefine the Fourier Principle as defining a process whereby $\mathbf{J_c}.\nabla T \leq 0$ is always true in any region of a system, where $\mathbf{J_c}$ is the *conductive* heat vector only, and in the absence of a temperature gradient, $\mathbf{J_c}$ is necessarily zero [29]. Consider a volume element where δn particles of species n passes through in unit time with a characteristic thermal transport energy QH (per particle or unit concentration) for the δn particles which occupy the volume element, having a non-equilibrium temperature T with respect to that whole volume element. We shall consider a new scheme for conserved flux quantities from the above modified Fourier Principle in the steady state only. Imagine that the species n moves through the lattice in the volume element in the steady state. The temperature may be determined by a "'diathermal fibre"' [8]. This "stationary" lattice will be responsible for the conductive heat transfer with respect to that moving subsystem, immediately implying that the "lattice" can therefore be other subsystems also in relative motion with the subsystem of interest. Since the temperature profile of the volume elements are approximated by Heavyside step functions, each of the subsystems must give up its thermal transport energy at the boundary of the lattice, and this becomes part of the conductive heat term. There are also dissipative processes which convert work energy into thermal energy at the boundaries when the concerned subsystem of particles is acted on by a field which does work on the subsystem. In unit time, the amount of heat dissipated to the boundary of the subsystem is written as $\alpha.\delta\phi.\delta n$ where $0 \leq \alpha \leq 1$ and where $\delta\phi$ is the change of potential energy of the field per unit number or mass of species n ; the$(1-\alpha)\delta\phi.\delta n$ remaining units of energy is not dissipated as heat and may be utilized via a motor device doing work on the external environment (such as in a standard thermocouple circuit). The external heat flux for the next adjacent volume element must come from the lattice conductive heat, given as $\dot{Q}_{ext}(x)$, and for 1-D (in the x direction) we write $\mathbf{J_c} = \dot{Q}_{ext}(x)$. Our modified Fourier principle demands that the conductive heat at the other boundary end with coordinates $x+\delta x$ and which is at a lower temperature than at point x must be the existing $\dot{Q}_{ext}(x)$ plus the dissipation due to force field (work) dissipation and the change in thermal energy:

$$\begin{aligned} \mathbf{J_c}(x+dx) &= \dot{Q}_{ext}(x)+\alpha\delta(\phi\delta n)+dQH_n\delta n \\ &= \mathbf{J_c}(x)+\alpha.\delta\phi.\delta n+dQH_n\delta n \end{aligned} \tag{39}$$

since $\delta(\delta n)$ is zero for conserved quantities, and where δx is a unit distance and $\delta\phi$ is the change in potential over this distance; dQH_n is the thermal transport energy per

particle or unit concentration for species n.

In order to relate the present formulation with the experimental set-ups which has been configured to the Onsager theory, it is important to relate the so-called entropy production in the volume element denoted by $\dot{\sigma}$ [31] (as opposed to that brought from the "outside") which is our theory where $\dot{\sigma} = \sum_i \dot{a}_i F_i = \sum_{ij} L^*_{ij} F_i F_j \geq 0$. The KCP viewpoint as defined in this work cannot suppose that there is any such "*internal*" entropy production, since there is no net energy transfer to a system in a volume element, and that volume element is at a fixed temperature. We thus form the entropy increase in terms of the increase due to the thermal interchange across the boundaries of the sub-elements, so that

$$\begin{aligned} \nabla.(\mathbf{J_c}/T) &= \dot{S} = \dot{\sigma} \\ &= \nabla.\mathbf{J_c}/T - (\mathbf{J_c}/T^2).\nabla.T \geq 0. \end{aligned} \tag{40}$$

From (39-40) and generalizing to 3-D and N particle quantities due to species n_i ($i = 1,2,...N$) we derive

$$\dot{\sigma} = \sum_i^N \alpha_i \delta n_i \delta \phi_i / T + \sum_i^N dQH_i \delta n_i / T - \mathbf{J_c}.(\nabla T / T^2)\delta x \tag{41}$$

where δx is the unit positive distance, dQH_i the thermal energy change per particle or unit concentration for species i, ϕ_i the change in force field potential per unit concentration . From the postulated inequality $\mathbf{J_c}.\nabla \leq 0$, we deduce $-\mathbf{J_c}.\nabla/T^2 \geq 0$. From (40-41)it follows that

$$\sum_i (\alpha_i \delta \phi_i \delta n_i / T + dQH_i \delta n_i / T) \geq 0\,. \tag{42}$$

In many first order expressions (such as Ohm's law) δn is positively proportional to $\delta \phi$ so that generally we can write two inequalities as follows:

$$-\mathbf{J_c}.\nabla/T^2 \geq 0\ ;\ \alpha_i \delta \phi_i \delta n_i / T \geq 0\,. \tag{43}$$

It can be shown that expressions (43) corresponds to the leading diagonal terms in the LIT expansions of the"*entropy production*" per unit volume i.e. $L^*_{jj} F_{jj}$. A major difference between the present work and LIT or other extensions thereof is that our $\mathbf{J_q} = \mathbf{J_c}$ is a composite term which is a function of the entire species flows and their energy interaction where a temperature is defined and thus applies directly to fluid thermodynamics also where a conventional "lattice" is deemed not to exist over a particular volume element, and is defined even when there is a net particle flux in a particular direction; the form $\mathbf{J_c}$ reduces to that of ordinary heat conduction (in solids) where there is no net particle flow. To complete the connection with LIT we proceed as follows. The complete set of independent variables for QH_i is denoted by the vector function $\mathbf{v}$, and it may of course include such variables as the potentials ϕ_i. Define the thermodynamical force F_i as

$$F_i = ((1/T)\partial QH_i / \partial \mathbf{v}).\delta \mathbf{v} \tag{44}$$

In (unit) time δt, we may express (41) by expanding dQH_i as in (44) to yield

$$\delta S = -(\mathbf{J_c}.\nabla T/T^2)\delta t + \sum_i \alpha_i \delta\phi_i \delta n_i/T + \sum_i \delta n_i F_i. \tag{45}$$

In LIT, the fundamental assumption is that the fluxes δn_i are a linear function of the forces F_i [12, eq. 1.11] where in fact we make a more general assumption by writing $\delta n_i = \delta n_i(F_1, F_2 .... F_N)$ where $\delta n_i(0) = 0$, so that to first order, we may write in unit time

$$\delta n_i = \sum_z^N L_{iz} F_z \text{ where } L_{iz} = \partial \delta n_i / \partial F_z|_{F=0}. \tag{46}$$

It has been demonstrated that $\sum_i \delta n_i dQH_i/T$ is a perfect differential [26] which is briefly recapitulated in (38) and neighboring paragraphs about this equation where the factor δn_i is derived from the fact that the present subsystem is not a fixed number of particles that traverses a circuit, but a portion of it which is contained in a fixed volume region common to all other flow quantities in that region. Since $\sum_i \delta n_i dQH_i/T$ is a perfect differential, then so must $\delta S'$, the contribution from the non-diagonal cross terms given by

$$\delta S' = \sum_i^N \delta n_i F_i \tag{47}$$

so that the (Maxwellian) perfect differential criterion yields

$$\frac{\partial \delta n_i}{\partial F_j} = \frac{\partial \delta n_j}{\partial F_i} \tag{48}$$

where within the LIT framework (46) and (48) gives

$$L_{iz} = L_{zi}. \tag{49}$$

This condition is only approximate. Eqn.(46) states that the forces F_j are to be considered "independent" and so we might expand to second order for greater accuracy to yield

$$\delta n_i = \sum_z L_{iz} F_z + \sum_j \sum_k K_{ijk} F_j F_k. \tag{50}$$

It can be proven that if L_{pi} is symmetric, then so is K_{ipz} in its indices [34].

CONCLUSIONS

The resume of results show that fundamental theories have been asserted and used extensively in physical description even if there is no compelling theoretical nor mathematical justification for these assertions. This is especially true of the assertion of time reversibility that is foundational to many theories in particle theories and thermodynamics.

Master equations in kinetics have been set up to maintain the detail balance and time reversibility arguments. Here, we illustrate from first principles that such ideas can be in contradiction to the basic definitions of probability theory.

Finally, we show that there are other ways to derive reciprocal relations from strict physical principles and postulates not shrouded in complex mathematics that are devoid of physical principles.

We conclude that there is a need for work that attempts to create non-competitive and community building concepts of basic principles and ideas that are open to modification and reinterpretation by all and for all times.

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